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<p>(1) International Application Number: PCT/JP93/00635 (2) International Filing Date: 14 May 1993 (14.05.93) (30) Priority data: 4/146771 14 May 1992 (14.05.92) JP (71) Applicant (for all designated States except US): JAPAN SYNTHETIC RUBBER CO., LTD. [JP/JP]; 2-11-24, Tsukiji, Chuo-ku, Tokyo 104 (JP). (72) Inventors; and (75) Inventors/Applicants (for US only): YASUDA, Kenji [JP/JP]; 150-9, Kariyo-cho 2-chome, Ushiku-shi, Ibaraki 300-12 (JP). ITO, Tetsuo [JP/JP]; 1733-15, Ohi, Kukizaki-machi, Inashiki-gun, Ibaraki 300-12 (JP). KURITA, Osamu [JP/JP]; Shofu-ryo, 1, Morigayama-cho, Yokkai-chi-shi, Mie 510 (JP).</p>		<p>(74) Agent: TSUKUNI, Hajime; Daiichi Shinwa Bldg., 10-8, Akasaka 2-chome, Minato-ku, Tokyo 107 (JP). (81) Designated States: AU, BB, BG, BR, CA, CZ, FI, HU, JP, KR, KZ, LK, MG, MN, MW, NO, NZ, PL, RO, RU, SD, SK, UA, US, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>
<p>(54) Title: PROCESS FOR PREPARATION OF OXYGEN PERMEABLE POLYMER MATERIAL (57) Abstract An oxygen permeable polymer material having both excellent oxygen permeability and good processability is provided. A process for the preparation of an oxygen permeable polymer material, which comprises polymerizing a mixture of a siloxanyl monomer having a polymerizable unsaturated bond and/or an acrylate type monomer and a compatible volatile organic solvent while removing a substantial portion of the organic solvent.</p>		

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DESCRIPTION

Process for preparation of oxygen permeable polymer material

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(Technical field)

This invention relates to a process for preparation of an oxygen permeable polymer material particularly useful as ophthalmic materials such as contact lenses and intraocular lenses.

10

(Background art)

Various plastic materials, for example, polymethyl methacrylate, have conventionally been used as ophthalmic materials such as contact lenses and intraocular lenses. However, conventional ophthalmic materials have problems that oxygen permeabilities are low and contaminants in tear and intraocular fluid are easily attached thereto so that, for example, when said materials are processed into contact lenses, such contact lenses cannot be worn continuously for a long time.

20

Thus, highly water-containing soft contact lenses comprising poly(N-vinyl-2-pyrrolidone) as a main component, which can be worn for a long time have been developed. However, such lenses have insufficient mechanical strength due to high water content thereof, and are required to be sterilized each time they are used as contact lenses, whereby handlings are extremely complicated.

30

On the other hand, as an ophthalmic material which does not have such drawbacks, attention has recently been paid to a non-water-containing ophthalmic material comprising a copolymer of siloxanyl monoacrylate or siloxanyl mono-

35

methacrylate and fluoroacrylate or fluoromethacrylate.

However, this material has a drawback that its properties change greatly depending on the copolymerization ratio of siloxanyl monoacrylate or siloxanyl monomethacrylate and fluoroacrylate or fluoromethacrylate. For example, when the copolymerization ratio of siloxanyl monoacrylate or siloxanyl monomethacrylate is made larger, oxygen permeability is improved, but there are problems that adsorption or attachment of contaminants are remarkable, and the material becomes too brittle and soft, whereby handlings are complicated in another sense. To the contrary, when the copolymerization ratio of fluoroacrylate or fluoromethacrylate is made larger, contaminants are hardly adsorbed or attached, but there is a problem that oxygen permeability is lowered.

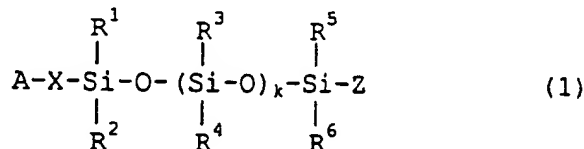
As a process for obtaining contact lenses having good oxygen permeability, a method in which a monomer component and a solvent having compatibility therewith are mixed, the mixture is poured into a mold and polymerized, and then the solvent is removed from the polymerized molded product has been proposed in JP-A-89-225913. In this process, all amount of the solvent is removed after completion of the polymerization. Thus, when the mixture is poured into a lens-shaped mold and polymerized, a predetermined lens shape cannot be maintained at the stage of removing the solvent, and when the mixture is polymerized so as to have a lump shape such as a rod shape and a block shape, it is difficult to maintain the shape in the beginning of the polymerization so that it is difficult to carry out mechanical processings such as cutting after the polymerization and also a step of removing the solvent is required after completion of the polymerization, whereby there are problems in operatability and economy.

(Disclosure of the invention)

Thus, an object of this invention is to provide an improved process for preparation of an oxygen permeable polymer material having both excellent oxygen permeability and excellent mechanical processability.

In order to solve the problems described above, the present inventors have studied intensively relations between processes for preparations of ophthalmic polymer materials comprising siloxanyl monoacrylate and/or siloxanyl monomethacrylate, and fluoroacrylate and/or fluoromethacrylate, and characteristics of said polymer materials, and consequently found that by removing a substantial portion of a volatile organic solvent having compatibility with a monomer component during polymerization of the monomer component in the presence of the volatile organic solvent, an oxygen permeable polymer material having both extremely excellent oxygen permeability and good processability can be obtained, to accomplish this invention.

That is, this invention comprises a process for preparation of an oxygen permeable polymer material, which comprises mixing a monomer component comprising one or more polymerizable monomer(s) represented by formula (1) shown below and/or one or more polymerizable monomer(s) represented by formula (2) shown below and one or more crosslinkable monomer(s) with a volatile organic solvent having compatibility, and then polymerizing the mixture while removing a substantial portion of the above volatile organic solvent from a polymerization system,



wherein A represents a polymerizable unsaturated group,

X represents a divalent hydrocarbon group or a divalent oxahydrocarbon group which is unsubstituted or substituted by hydroxy group, preferably a C₁ to C₁₀ alkylene group or a C₄ to C₁₀ oxaalkylene group unsubstituted or substituted

5 by hydroxy group,

R¹, R², R³, R⁴, R⁵ and R⁶ may be the same or different from each other and each represent an alkyl group, a fluoroalkyl group, a phenyl group, a vinyl group, a hydrogen atom, provided that R¹ and R², R³ and R⁴ or R⁵ and R⁶ cannot be

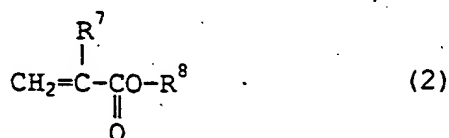
10 hydrogen atoms at the same time,

or a group of formula:
$$\begin{array}{c} Y^1 \\ | \\ -\text{OSi}-Y^2 \\ | \\ Y^3 \end{array}$$

where Y¹, Y² and Y³ may be the same or different from each other and are each an alkyl group, a fluoroalkyl group, a phenyl group, a vinyl group or a hydrogen atom, provided
15 that the case where no less than two of Y¹, Y² and Y³ are hydrogen atoms is excluded,

Z represents an alkyl group, a fluoroalkyl group, a tri-alkylsilylalkylene group or a hydrogen atom, and

k is an integer from 0-100, preferably 0-20,



20

wherein R⁷ represents an alkyl group, a fluoroalkyl group, a fluorine atom or a hydrogen atom, and

R⁸ represents a hydrogen atom or an alkyl group, preferably a C₁ to C₂₀ alkyl group; or a fluoroalkyl group; preferably
25 a C₁ to C₂₀ fluoroalkyl group bonded through a divalent

hydrocarbon group, preferably a C₁ to C₄ hydrocarbon group; or an aminoalkyl, hydroxyalkyl or epoxyalkyl group; preferably a C₁ to C₁₀ aminoalkyl, a C₁ to C₁₀ hydroxyalkyl or a C₁ to C₁₀ epoxyalkyl group; a C₃ to C₈ monocyclic or a C₈ to
30 C₁₆ bi- or tricyclic hydrocarbon group; an arylalkyl group; or an aryl group.

(Best modes for practicing the invention)

In the following, this invention is described in detail,
and the object, constitution and effect of this invention
5 will be clarified thereby.

In the polymerizable monomer represented by formula (1) to
be used in this invention, the polymerizable unsaturated
group A includes, for example, a vinyl group represented by
10 formula $\text{CH}_2=\text{CH}-$, an acryloxy group or methacryloxy group
represented by formula $\text{CH}_2=\text{C}(\text{R})\text{COO}-$ (where R is a methyl
group, a fluoromethyl group, a fluorine atom or a hydrogen
atom), an acrylamide group represented by formula $\text{CH}_2=\text{CH}-$
 $\text{CONH}-$, a styryl group represented by formula $\text{CH}_2=\text{CHC}_6\text{H}_4-$,
15 an acrylonitrile group represented by formula $\text{CH}_2=\text{C}(\text{CN})-$
and a 2-cyanoacryloxy group represented by formula
 $\text{CH}_2=\text{C}(\text{CN})\text{COO}-$.

X in formula (1) includes a divalent hydrocarbon group or a
20 divalent oxahydrocarbon group which is unsubstituted or
substituted by hydroxy group, preferably a C_1 to C_{10} alkyl-
ene group or a C_4 to C_{10} oxaalkylene group unsubstituted or
substituted by hydroxy group, for example, a methylene
group, an ethylene group, a propylene group, a butylene
25 group, a pentylene group, a hexylene group, a heptylene
group and an octylene group, and the divalent hydrocarbon
group of R^8 in formula (2) includes a C_1 to C_4 alkylene
group such as a methylene group, an ethylene group, a
propylene group and a butylene group; a glycerol group and
30 a propylglycerol group.

Further, in R^1 to R^6 , Y^1 to Y^3 and Z in formula (1) and R^7
and R^8 in formula (2), the alkyl group includes, for exam-
ple, linear or branched alkyl groups, preferably $\text{C}_1 - \text{C}_{20}$
35 linear or branched alkyl, more preferably $\text{C}_1 - \text{C}_{10}$ linear
or branched alkyl, further preferably $\text{C}_1 - \text{C}_5$ linear or

- branched alkyl, such as a methyl group, an ethyl group, an n-propyl group, an isopropyl group, an n-butyl group, an isobutyl group, a sec-butyl group, a t-butyl group, an n-pentyl group, an isopentyl group, a neo-pentyl, a hexyl group, a heptyl group, an octyl group, a 2-ethylhexyl group, a nonyl group, a decyl group, an undecyl group and a dodecyl group, and the fluoroalkyl group includes, for example, linear or branched fluoroalkyl groups, preferably C₁ - C₂₀ linear or branched fluoroalkyl, more preferably C₁ - C₁₀ linear or branched fluoroalkyl, further preferably C₂ - C₅ linear or branched fluoroalkyl, such as a trifluoromethyl group, a trifluoroethyl group, a trifluoropropyl group, a pentafluorobutyl group, a heptafluoropentyl group and a nonafluorohexyl group. R¹ to R⁶ or Y¹ to Y³ in formula (1) and R⁷ and R⁸ in formula (2) may be the same or different from each other, respectively and when k in formula (1) is 2-100, plural -Si(R³)(R⁴)-O- groups may be the same or different from each other.
- Specific examples of the polymerizable monomer represented by formula (1) include siloxanyl monomethacrylates or siloxanyl monoacrylates such as pentamethyldisiloxanylmethyl methacrylate, pentamethyldisiloxanylmethyl acrylate, pentamethyldisiloxanylpropyl methacrylate, pentamethyldisiloxanylpropyl acrylate, methylbis(trimethylsiloxy)silylpropyl methacrylate, methylbis(trimethylsiloxy)silylpropyl acrylate, tris(trimethylsiloxy)silylpropyl methacrylate, tris(trimethylsiloxy)silylpropyl acrylate, methylbis(trimethylsiloxy)silylpropylglycerol methacrylate, methylbis(trimethylsiloxy)silylpropylglycerol acrylate, tris(trimethylsiloxy)silylpropylglycerol methacrylate, tris(trimethylsiloxy)silylpropylglycerol acrylate, mono(methylbis(trimethylsiloxy)siloxy)bis(trimethylsiloxy)silylpropylglycerol methacrylate, mono(methylbis(trimethylsiloxy)siloxy)bis(trimethylsiloxy)silylpropylglycerol acrylate, trimethylsilylethyltetramethyldisiloxanylpropylglycerol

methacrylate and trimethylsilylethyltetramethyldisiloxanyl-propylglycerol acrylate; and
fluorosiloxanyl monomethacrylates or fluorosiloxanyl mono-
acrylates such as (3,3,3-trifluoropropyldimethylsiloxy)bis-
5 (trimethylsiloxy)silylmethyl methacrylate, (3,3,3-tri-
fluoropropyldimethylsiloxy)bis(trimethylsiloxy)silylmethyl
acrylate, (3,3,4,4,5,5,5-heptafluoropentyldimethylsiloxy)-
(methylbis(trimethylsiloxy)siloxy)trimethylsiloxypropyl
10 methacrylate and (3,3,4,4,5,5,5-heptafluoropentyldi-
methylsiloxy) (methylbis(trimethylsiloxy)siloxy)trimethyl-
siloxypropyl acrylate.

Next, specific examples of the polymerizable monomer repre-
sented by formula (2) include fluoromethacrylates or
15 fluoroacrylates such as 2,2,2-trifluoroethyl methacrylate,
2,2,2-trifluoroethyl acrylate, 2,2,2-trifluoroethyl- α -
fluoroacrylate, 2,2,2-trifluoroethyl- α -trifluoromethyl
acrylate, 2,2,3,3-tetrafluoropropyl methacrylate, 2,2,3,3-
tetrafluoropropyl acrylate, 2,2,3,3,3-pentafluoropropyl
20 methacrylate, 2,2,3,3,3-pentafluoropropyl acrylate, 2,2,2,
2',2',2'-hexafluoroisopropyl methacrylate, 2,2,2,2',2',2'-
hexafluoroisopropyl acrylate, 2,2,3,4,4,4-hexafluorobutyl
methacrylate, 2,2,3,4,4,4-hexafluorobutyl acrylate, 2,2,
3,3,4,4,5,5-octafluoropentyl methacrylate, 2,2,3,3,4,4,
25 5,5-octafluoropentyl acrylate, 2,2,3,3,4,4,5,5,6,6,7,7-
dodecafluoroheptyl methacrylate, 2,2,3,3,4,4,5,5,6,6,7,7-
dodecafluoroheptyl acrylate, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,
9,9-hexadecafluorononyl methacrylate, 2,2,3,3,4,4,5,5,6,6,
7,7,8,8,9,9-hexadecafluorononyl acrylate, 3,3,4,4,5,5,6,6,
30 7,7,8,8,8-tridecafluorooctyl methacrylate, 3,3,4,4,5,5,
6,6,7,7,8,8,8-tridecafluorooctyl acrylate, 2,2,3,3-tetra-
fluoro-1-methylpropyl methacrylate, 2,2,3,3-tetrafluoro-1-
methylpropyl acrylate, 2,2,3,3-tetrafluoro-1,1-dimethyl-
propyl methacrylate, 2,2,3,3-tetrafluoro-1,1-dimethylpropyl
35 acrylate, 2,2,3,3,4,4,5,5-octafluoro-1,1-dimethylpentyl
methacrylate and 2,2,3,3,4,4,5,5-octafluoro-1,1-dimethyl-

pentyl acrylate;

alkyl methacrylates or alkyl acrylates such as methyl methacrylate, methyl acrylate, ethyl methacrylate, ethyl acrylate, isopropyl methacrylate, isopropyl acrylate, n-butyl methacrylate, n-butyl acrylate, t-butyl methacrylate, t-butyl acrylate, cyclohexyl methacrylate, cyclohexyl acrylate, benzyl methacrylate, benzyl acrylate, isobornyl methacrylate and isobornyl acrylate;

10 α -alkylacrylic acids or α -fluoroalkylacrylic acids such as (α -ethyl)acrylic acid, (α -butyl)acrylic acid, (α -trifluoroethyl)acrylic acid, (α -trifluoropropyl)acrylic acid and (α -nonafluorohexyl)acrylic acid;

15 alkyl(α -alkyl) acrylates such as methyl-(α -ethyl) acrylate, ethyl-(α -ethyl) acrylate, propyl-(α -ethyl) acrylate, butyl-(α -ethyl) acrylate, 2-hydroxyethyl-(α -ethyl) acrylate, 2-hydroxypropyl-(α -ethyl) acrylate, diethylaminoethyl-(α -ethyl) acrylate, glycidyl-(α -ethyl) acrylate, methyl-(α -butyl) acrylate, ethyl-(α -butyl) acrylate, propyl-(α -butyl) acrylate, butyl-(α -butyl) acrylate, 2-hydroxyethyl-(α -butyl) acrylate, 2-hydroxypropyl-(α -butyl) acrylate, diethylaminoethyl-(α -butyl) acrylate and glycidyl-(α -butyl) acrylate;

25 alkyl(α -fluoroalkyl) acrylates such as methyl-(α -trifluoroethyl) acrylate, ethyl-(α -trifluoroethyl) acrylate, propyl-(α -trifluoroethyl) acrylate, butyl-(α -trifluoroethyl) acrylate, methyl-(α -trifluoropropyl) acrylate, ethyl-(α -trifluoropropyl) acrylate, propyl-(α -trifluoropropyl) acrylate, butyl-(α -trifluoropropyl) acrylate, methyl-(α -nonafluorohexyl) acrylate, ethyl-(α -nonafluorohexyl) acrylate, propyl-(α -nonafluorohexyl) acrylate and butyl-(α -nonafluorohexyl) acrylate; and

35 fluoroalkyl(α -fluoroalkyl) acrylates such as 2,2,2-trifluoroethyl-(α -trifluoroethyl) acrylate, 2,2,3,3-tetrafluoropropyl-(α -trifluoroethyl) acrylate, 2,2,3,3,3-pentafluoropropyl-(α -trifluoroethyl) acrylate, 2,2,2,2',2',2'-hexafluoroisopropyl-(α -trifluoroethyl) acrylate, 2,2,3,

- 4,4,4-hexafluorobutyl-(α -trifluoroethyl) acrylate, 2,2,3,3,4,4,5,5-octafluoropentyl-(α -trifluoroethyl) acrylate, 2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl-(α -trifluoroethyl) acrylate, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9-hexadecafluorononyl-(α -trifluoroethyl) acrylate, 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-(α -trifluoroethyl) acrylate, 2,2,3,3-tetrafluoro-1-methylpropyl-(α -trifluoroethyl) acrylate, 2,2,3,3-tetrafluoro-1,1-dimethylpropyl-(α -trifluoroethyl) acrylate, 2,2,3,3,4,4,5,5-octafluoro-1,1-dimethylpentyl-(α -trifluoroethyl) acrylate, 2,2,2-trifluoroethyl-(α -nonafluorohexyl) acrylate, 2,2,3,3,3-pentafluoropropyl-(α -nonafluorohexyl) acrylate, 2,2,2,2,2-hexafluoroisopropyl-(α -nonafluorohexyl) acrylate, 2,2,3,4,4,4-hexafluorobutyl-(α -nonafluorohexyl) acrylate, 2,2,3,3,4,4,5,5-octafluoro-pentyl-(α -nonafluorohexyl) acrylate, 2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl-(α -nonafluorohexyl) acrylate, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9-hexadecafluorononyl-(α -nonafluorohexyl) acrylate, 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-(α -nonafluorohexyl) acrylate, 2,2,3,3-tetrafluoro-1-methylpropyl-(α -nonafluorohexyl) acrylate, 2,2,3,3-tetrafluoro-1,1-dimethylpropyl-(α -nonafluorohexyl) acrylate, 2,2,3,3,4,4,5,5-octafluoro-1,1-dimethylpentyl-(α -nonafluorohexyl) acrylate, 2,2,2-trifluoroethyl-(α -penta-decafluorononyl) acrylate and 2,2,3,3,3-pentafluoropropyl-(α -pentadecafluorononyl) acrylate.

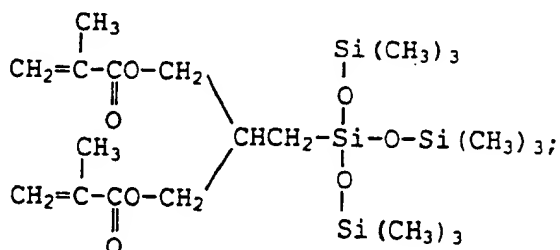
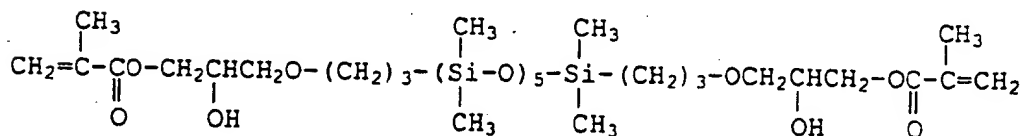
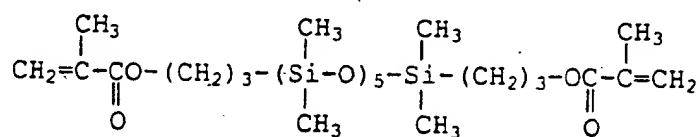
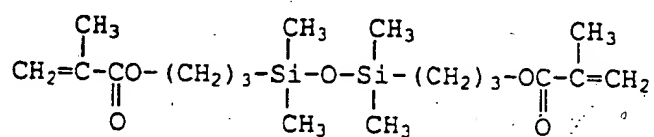
- Among the polymerizable monomers represented by formula (1) or (2), preferred monomers are siloxanyl monomethacrylates or siloxanyl monoacrylates such as pentamethyldisiloxanylmethyl methacrylate, pentamethyldisiloxanylmethyl acrylate, pentamethyldisiloxanylpropyl methacrylate, pentamethyldisiloxanylpropyl acrylate, methylbis(trimethylsiloxy)silylpropyl methacrylate, methylbis(trimethylsiloxy)silylpropyl acrylate, tris(trimethylsiloxy)silylpropyl methacrylate and tris(trimethylsiloxy)silylpropyl acrylate; fluorosiloxanyl methacrylates or fluorosiloxanyl acrylates

such as (3,3,3-trifluoropropyldimethylsiloxy)bis(trimethylsiloxy)silylmethyl methacrylate, (3,3,3-trifluoropropyldimethylsiloxy)bis(trimethylsiloxy)silylmethyl acrylate, (3,3,4,4,5,5,5-heptafluoropentyldimethylsiloxy) (methylbis-
5 (trimethylsiloxy)siloxy)trimethylsiloxypropyl methacrylate and (3,3,4,4,5,5,5-heptafluoropentyldimethylsiloxy) (methylbis(trimethylsiloxy)siloxy)trimethylsiloxypropyl acrylate;
fluoromethacrylates or fluoroacrylates such as 2,2,2-tri-
10 fluoroethyl methacrylate, 2,2,2-trifluoroethyl- α -fluoroacrylate, 2,2,2-trifluoroethyl- α -trifluoromethyl acrylate, 2,2,3,3-tetrafluoropropyl methacrylate, 2,2,3,3,3-pentafluoropropyl methacrylate, 2,2,2,2',2',2'-hexafluoroisopropyl methacrylate, 2,2,3,4,4,4-hexafluorobutyl methacrylate,
15 2,2,3,3,4,4,5,5-octafluoropentyl methacrylate, 2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl methacrylate, 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl methacrylate, 2,2,3,3-tetrafluoro-1-methylpropyl methacrylate, 2,2,3,3-tetrafluoro-1,1-dimethylpropyl methacrylate and 2,2,3,3,4,4,5,5-octafluoro-1,1-dimethylpentyl methacrylate; and
20 alkyl methacrylates or alkyl acrylates such as methyl methacrylate, methyl acrylate, ethyl methacrylate, ethyl acrylate, isopropyl methacrylate, isopropyl acrylate, n-butyl methacrylate, n-butyl acrylate, t-butyl methacrylate, t-
25 butyl acrylate, cyclohexyl methacrylate, cyclohexyl acrylate, benzyl methacrylate, benzyl acrylate, isobornyl methacrylate and isobornyl acrylate.

The crosslinkable monomer in this invention is a poly-
30 functional compound having two or more polymerizable unsaturated groups which can be copolymerized with the polymerizable monomer represented by formula (1) or formula (2). However, this crosslinkable monomer does not include a compound having a vinyl group bonded to an Si atom among
35 the polymerizable monomers represented by formula (1).

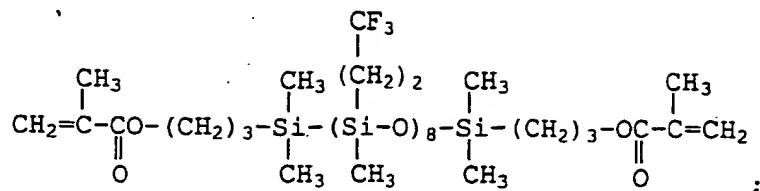
Specific examples of the above crosslinkable monomer include polyfunctional methacrylates or polyfunctional acrylates each having or not having a fluorine atom, such as ethylene glycol dimethacrylate, ethylene glycol diacrylate, diethylene glycol dimethacrylate, diethylene glycol diacrylate, triethylene glycol dimethacrylate, triethylene glycol diacrylate, tetraethylene glycol dimethacrylate, tetraethylene glycol diacrylate, propylene glycol dimethacrylate, propylene glycol diacrylate, 1,4-butanediol dimethacrylate, 1,4-butanediol diacrylate, neopentyl glycol dimethacrylate, neopentyl glycol diacrylate, trimethylolpropane trimethacrylate, trimethylolpropane triacrylate, bisphenol A dimethacrylate, bisphenol A diacrylate, bis(trifluoromethyl) bisphenol A dimethacrylate and bis(trifluoromethyl) bisphenol A diacrylate; and silicone type polyfunctional compounds represented by formulae shown below.

Siloxanyl dimethacrylates of

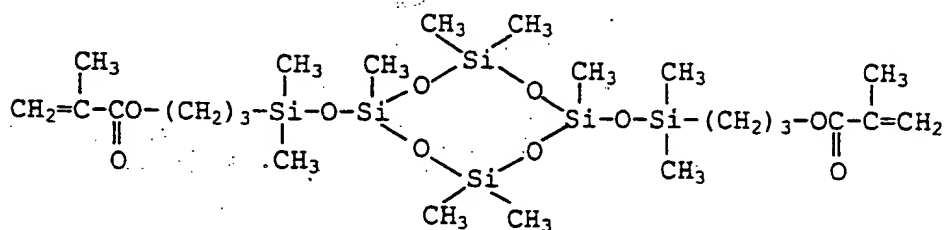


fluorosiloxanyl dimethacrylates of

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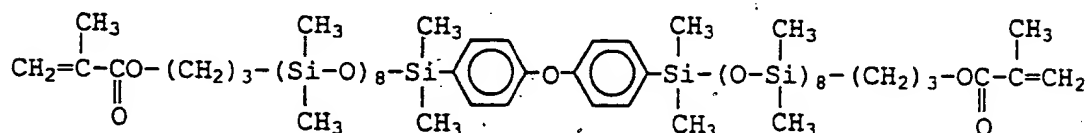


dimethacrylates having cyclic siloxane groups of

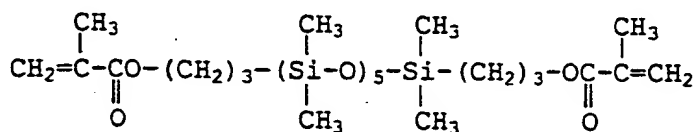
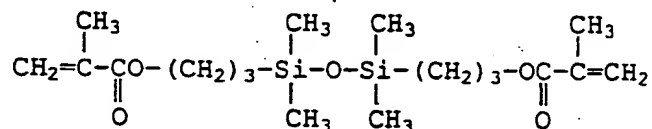


5 and

siloxanyl dimethacrylates having bisphenol A ether groups of

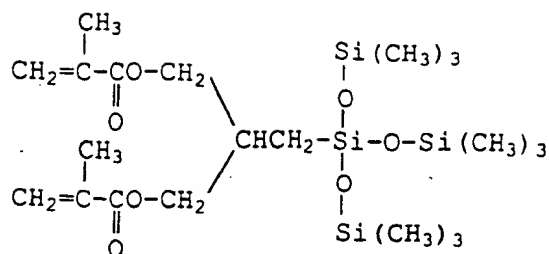


- 10 Among the above crosslinkable monomers, preferred monomers are polyfunctional methacrylates such as ethylene glycol dimethacrylate, diethylene glycol dimethacrylate, propylene glycol dimethacrylate, 1,4-butanediol dimethacrylate, neopentyl glycol dimethacrylate, trimethylolpropane trimethacrylate and bisphenol A dimethacrylate; and siloxanyl dimethacrylates of
- 15



and

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The copolymerization ratio of the polymerizable monomer(s) represented by formula (e) (1) and/or (2) and the crosslinkable monomer in this invention is generally 99.5/0.5 to 5/95, preferably 99/1 to 10/90 in terms of weight ratio. However, when the polymerizable monomer represented by formula (1) is used and said monomer has a vinyl group bonded to an Si atom, this vinyl group can be also polymerized so that it is desired that the copolymerization ratio of the above crosslinkable monomer is controlled depending on the desired crosslinking degree of a polymer material to be obtained.

Further, in this invention, a polymerizable monomer other than the above-mentioned may be used in combination, if desired. In that case, for example, by using a hydrophilic monomer such as acrylic acid, methacrylic acid, vinyl pyridine, N-vinyl-2-pyrrolidone and 2-hydroxyethyl methacrylate, hydrophilicity can be imparted on the surface of a polymer material to be obtained.

The volatile organic solvent in this invention is an organic solvent which does not substantially inhibit polymerization reaction nor participate the reaction and has compatibility. Here, the compatibility means compatibility with both the monomer component and the resulting copolymer. As such an organic solvent, preferred are those having a boiling point of 150°C or lower.

Specific examples of the above volatile organic solvent

include saturated hydrocarbons such as n-pentane, n-hexane, n-heptane, 2-methylhexane, 2,4-dimethylpentane, cyclopentane and methylcyclopentane; unsaturated hydrocarbons such as 1-hexene, 1-heptene, cyclohexene, benzene and toluene; 5 halogenated hydrocarbons such as dichloromethane, chloroform, carbon tetrachloride, fluorobenzene and hexafluorobenzene; ethers such as diethyl ether, diisopropyl ether, ethyl vinyl ether and tetrahydrofuran; and acetates such as ethyl acetate, n-propyl acetate and n-butyl acetate.

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The volatile organic solvents in this invention may be used singly or in combination of two or more kinds.

15 The amount of the volatile organic solvent to be used in this invention is generally 5-200 parts by weight, preferably 5-100 parts by weight based on 100 parts by weight of all monomer component. If the amount of the volatile organic solvent to be used is less than 5 parts by weight, oxygen permeability of a polymer material obtained may not 20 be improved sufficiently, while if it exceeds 200 parts by weight, a polymer material obtained by polymerization may be easily deformed by shrinkage to lower processability.

25 The polymerization in this invention is carried out generally by radical polymerization, and there may be used methods such as

① a method in which polymerization is carried out by using a thermal polymerization initiator such as benzoyl peroxide and azobisisobutyronitrile, for example, in an 30 amount of 0.01-5 parts by weight based on 100 parts by weight of all monomer component and, if necessary, raising a polymerization temperature stepwise,

② a method in which polymerization is carried out by using a photopolymerization initiator such as benzoin, 35 benzophenone and Michler's ketone, for example, in an amount of 0.01-5 parts by weight based on 100 parts by

weight of all monomer component, irradiating UV rays and, if necessary, raising a polymerization temperature stepwise,

③ a method in which polymerization is carried out by using a thermal polymerization initiator and a photopolymerization initiator in combination under irradiation of UV rays and, if necessary, raising a polymerization temperature stepwise,

④ a method in which polymerization is carried out under irradiation of, e.g. UV rays.

When polymerization is carried out in the presence of a thermal polymerization initiator by raising a polymerization temperature stepwise, two or more kinds of thermal polymerization initiators having different decomposition temperatures may be used in combination.

In this invention, it is preferred that polymerization is carried out by using a thermal polymerization initiator and a photopolymerization initiator in combination, irradiating UV rays under atmosphere of an inactive gas such as nitrogen, and raising a polymerization temperature stepwise.

Polymerization is preferably carried out at a temperature ranging from 0 to 150 °C and, in the initial polymerization stage, preferably at a temperature ranging from 0 to 30 °C. It is also preferred to raise the temperature gradually from the intermediate stage to the final stage of the polymerization. Polymerization is preferably carried out at atmospheric pressure. Polymerization time depends on the rate-determining step. An inert gas, e.g. nitrogen gas may be passed through to remove volatile organic solvents, even after termination of polymerization. In total, 4 to 48 hours are usually preferred. When a volatile organic solvent is evaporated during polymerization in the stream of an inert gas, such as nitrogen, the velocity of gas flow is preferably 0.1 to 1 liter/min in the initial polymerization

stage, and the gas flow may be gradually increased towards the final polymerization stage, e.g. to about 5 liter/min.

In this invention, the polymerization while removing a substantial portion of the volatile organic solvent from a polymerization system means that at least 70 % by weight or more, preferably 80 % by weight or more of the solvent mixed with the monomer component before initiation of polymerization is removed during polymerization. The solvent still remaining after the polymerization can be removed almost completely by a suitable method such as a method of volatilization under reduced pressure and a method of evaporation by heating.

When a substantial portion of the volatile organic solvent is removed from a polymerization system, there may be used, for example, (a) a method in which the solvent is removed continuously during polymerization, (b) a method in which the solvent is removed stepwise during polymerization. In the case of (a), the removing rate of the solvent may be constant, or the removing rate of the solvent may be increased or decreased gradually. In the case of (b), the removing rate of the solvent may be the same at the respective stages, it may be increased successively or decreased successively at the respective stages, or further the removing rate may be the highest or the lowest at the middle stage of polymerization among the respective stages. These methods of removing the volatile organic solvent may be selected and practiced suitably in consideration of a monomer composition, a desired size or distribution of holes of a polymer material to be obtained, and a kind and an amount of the solvent.

In this invention, a polymerization vessel or polymerization device which can remove the volatile organic solvent during polymerization should be used. Such a polymeriza-

tion vessel or polymerization device includes, for example, those having gaps through which the above organic solvent can be volatilized during polymerization, or those which are tightly sealed, but can be opened at a suitable stage during polymerization.

A method of carrying out polymerization while removing a volatile organic solvent has conventionally been used as a method of controlling a polymerization temperature in general solution polymerization and precipitation polymerization, using an organic solvent. However, said method is a technique which has not yet been attempted in the preparation of an oxygen permeable polymer material such as ophthalmic materials, which require precision processing.

In this invention, as clarified in Examples and Comparative examples described below, by carrying out polymerization while removing a substantial portion of the volatile organic solvent, it is possible to obtain a polymer material in which not only oxygen permeability is highly improved, but also machinability and polishability which are indispensable for processing precision molded products such as contact lenses and intraocular lenses. Further, removal of the volatile organic solvent is carried out mainly from a monomer stage to a prepolymer stage (i.e. a partial polymerization stage) so that occurrence of distortion of a polymer material accompanied with removal of the solvent can be inhibited, and a step of removing the solvent after polymerization is not required or said step is simplified, whereby preparation steps of an oxygen permeable polymer material can be greatly rationalized.

The polymerization in this invention can be carried out by, for example, a process for the preparation of a copolymer with a lump shape in which a mixture of a monomer component and a volatile organic solvent is polymerized while remov-

ing a substantial portion of the volatile organic solvent. In that case, the copolymer with a lump shape obtained is cut and polished into a predetermined shape such as contact lenses and intraocular lenses.

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The polymer material obtained according to this invention exhibits machinability and polishability similar to those of conventional hard lenses comprising polymethyl methacrylate. Thus, the polymer material can be easily processed into a molded product with a predetermined shape (e.g. contact lenses, intraocular lenses), and also it is rigid and has extremely excellent oxygen permeability.

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Further, when the polymer material obtained according to this invention is used for contact lenses and intraocular lenses, in which fittings with tear and intraocular fluid are required, it is preferred that after processing into a predetermined shape, hydrophilicity is imparted to the surface by alkaline treatment, plasma treatment using, e.g. oxygen and nitrogen, plasma polymerization treatment using a hydrophilic group-containing compound, vapor deposition, sputtering or ion plating treatment using, e.g. an inorganic oxide, or the like.

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25 (Examples)

In the following, specific embodiments and effects of this invention are described in more detail by referring to Examples and Comparative examples, but this invention is not limited only by these Examples.

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In these Examples and Comparative examples, tests of oxygen permeability, visible light transmission and processabilities are conducted as described below.

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Oxygen permeability:

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The polymer material is processed into contact lenses and measured at 35°C in a 0.9 % by weight physiological saline solution by using a scientific research type film oxygen permeation meter manufactured by Rika Seiki Kogyo.

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Visible light transmission:

Discs comprising the polymer material (thickness: 0.2 mm, diameter: 15 mm) are measured at a wavelength of 500-600 nm by using a double beam spectrophotometer Model 200-20 manufactured by Hitachi, Ltd.

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Processabilities:

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Machinability

- O - Cut surface has luster
- Δ - Cut surface has luster, but is slightly opaque
- X - Cut surface is rough and whitened

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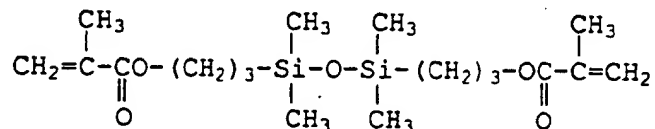
Polishability

- O - Polished surface has good luster
- Δ - Uneven polishing occurs
- X - Polished surface is rough and whitened

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Example 1

35 parts by weight of siloxanyl dimethacrylate of formula



20 parts by weight of 2,2,2-trifluoroethyl methacrylate, 30 parts by weight of methyl methacrylate, 50 parts by weight of n-hexane, and 0.1 part by weight of benzoin methyl ether and 0.1 part by weight of azobisisobutyronitrile as polymerization initiators are mixed sufficiently at room tem-

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- 20 -

perature, and the mixture is poured into a polymerization vessel made of polyethylene (radius: 2 cm, height: 4 cm) of which the upper side is opened. This polymerization vessel is placed in another polymerization vessel (inner volume: 5 500 cm³) to which nitrogen can be introduced. While flowing nitrogen at a flow rate of 1 liter/min, UV rays are irradiated at room temperature for 16 hours, and then polymerization is carried out at 40°C for 8 hours, at 80°C for 8 hours and 120°C for 12 hours. During this polymerization 10 process, substantially all amount of n-hexane is volatilized by accompaniment with flow of nitrogen.

After completion of the polymerization, the copolymer obtained is cut and polished to be processed into contact 15 lenses and discs, and the tests are conducted, respectively. The test results are shown in Table 1.

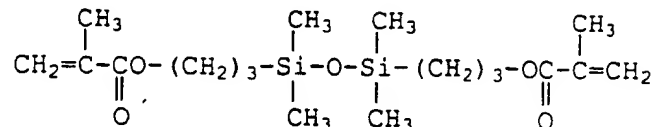
Example 2

20 40 parts by weight of tris(trimethylsiloxy)silylpropyl methacrylate, 5 parts by weight of 2,2,2,2',2',2'-hexafluoroisopropyl methacrylate, 30 parts by weight of methyl methacrylate, 5 parts by weight of ethylene glycol dimethacrylate, 10 parts by weight of ethyl(α -nonafluorohexyl) 25 acrylate, 5 parts by weight of methacrylic acid, 80 parts by weight of fluorobenzene, and 0.1 part by weight of benzoin methyl ether and 0.1 part by weight of azobisisobutyronitrile as polymerization initiators are mixed sufficiently at room temperature, and then the mixture is polymerized in the same manner as in Example 1. After completion of the polymerization, the copolymer is cut and polished to be processed into contact lenses and discs, and the tests are conducted. The test results are shown in 30 Table 1.

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Comparative example 1 (without solvent)

35 parts by weight of siloxanyl dimethacrylate of formula:



- 5 20 parts by weight of 2,2,2-trifluoroethyl methacrylate, 30 parts by weight of methyl methacrylate, and 0.1 part by weight of benzoin methyl ether and 0.1 part by weight of azobisisobutyronitrile as polymerization initiators are mixed sufficiently at room temperature, and the mixture is
- 10 polymerized in the same manner as in Example 1. After completion of the polymerization, the copolymer is cut and polished to be processed into contact lenses and discs, and the tests are conducted. The test results are shown in Table 1.

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Comparative example 2

- A reaction mixture having the same composition as that of Example 1 is poured into a glass tube and replacement with
- 20 nitrogen is carried out. In the same manner as in Example 1 except for not removing n-hexane during polymerization, polymerization is carried out to obtain a copolymer block. Thereafter, the copolymer block is dried under vacuum at
- 25 120°C for 48 hours to remove n-hexane. The copolymer block after removing n-hexane is deformed greatly and cannot maintain its columnar shape, whereby it is impossible to mount it on a lathe for cutting.

Table 1

	Example 1	Example 2	Comparative example 1
Oxygen permeability (*)	145	150	98
Visible light transmission (%)	92	92	90
Processability			
·Machinability	○	○	○
·Polishability	○	○	△

(*) unit: 10^{-11} cc·cm/cm³·sec·mmHg

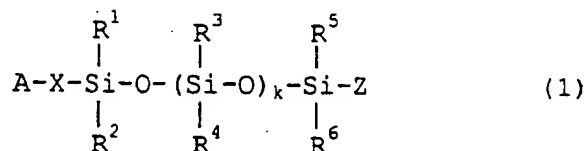
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(Utilizability in industry)

The oxygen permeable polymer material obtained according to the method of this invention has extremely high oxygen permeability and also excellent machinability and polishability. Further, in this invention, a substantial portion of a volatile organic solvent is removed during polymerization so that a step of removing a solvent after polymerization is not required or a step of removing a solvent can be simplified. Thus, the oxygen permeable polymer material obtained according to this invention is extremely useful as ophthalmic materials which require precision processing such as contact lenses and intraocular lenses, and according to this invention, such ophthalmic materials can be prepared extremely rationally.

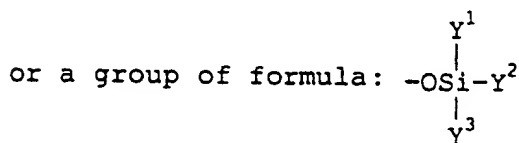
CLAIMS

1. A process for preparation of an oxygen permeable polymer material, which comprises mixing a monomer component comprising one or more polymerizable monomer(s) represented by formula (1) shown below and/or one or more polymerizable monomer(s) represented by formula (2) shown below and one or more crosslinkable monomer(s) with a volatile organic solvent having compatibility, and then polymerizing the mixture while removing a substantial portion of the volatile organic solvent from a polymerization system,



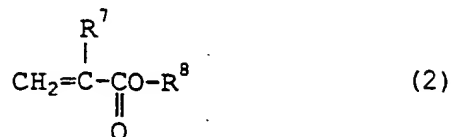
wherein A represents a polymerizable unsaturated group,

- 15 X represents a divalent hydrocarbon group or a divalent oxahydrocarbon group which is unsubstituted or substituted by hydroxy,
 R¹, R², R³, R⁴, R⁵ and R⁶ may be the same or different from each other and each represent an alkyl group, a fluoroalkyl group, a phenyl group, a vinyl group, a hydrogen atom, provided that R¹ and R², R³ and R⁴ or R⁵ and R⁶ cannot be hydrogen atoms at the same time,



- 25 where Y¹, Y² and Y³ may be the same or different from each other and are each an alkyl group or a fluoroalkyl group, a phenyl group, a vinyl group or a hydrogen atom, provided that the case where no less than two of Y¹, Y² and Y³ are hydrogen atoms is excluded,
 Z represents an alkyl group, a fluoroalkyl group, a trialkylsilylalkylene group or a hydrogen atom, and

k is an integer from 0-100,



wherein R⁷ represents an alkyl group, a fluoroalkyl group, a fluorine atom or a hydrogen atom, and R⁸ represents a hydrogen atom, an alkyl group, a fluoroalkyl group, an aminoalkyl group, a hydroxyalkyl group, an epoxyalkyl group, a monocyclic hydrocarbon group, a bi- or tricyclic hydrocarbon group, an arylalkyl group, or an aryl group.

2. A process according to claim 1, wherein at least 70 % by weight or more of the solvent mixed with the monomer component before initiation of polymerization is removed during polymerization.

3. A process according to claim 1, wherein at least 80 % by weight or more of the solvent mixed with the monomer component before initiation of polymerization is removed during polymerization.

4. A process according to claim 1, wherein the solvent is removed continuously during polymerization.

5. A process according to claim 1, wherein the solvent is removed stepwise during polymerization.

6. A process according to claim 1, wherein the polymerizable unsaturated group of A is one selected from a vinyl group represented by formula CH₂=CH-; an acryloxy group or methacryloxy group represented by formula CH₂=C(R)COO- where R is a methyl group, a fluoromethyl group, a fluorine atom or a hydrogen atom; an acrylamide group represented by formula CH₂=CHCONH-; a styryl group represented by formula

$\text{CH}_2=\text{CHC}_6\text{H}_4-$; an acrylonitrile group represented by formula $\text{CH}_2=\text{C}(\text{CN})-$ and a 2-cyanoacryloxy group represented by formula $\text{CH}_2=\text{C}(\text{CN})\text{COO}-$.

5 7. A process according to claim 1, wherein X is a methylene group, an ethylene group, a propylene group, a butylene group, a pentylene group, a hexylene group, a heptylene group, an octylene group, a glycerol group or a propylglycerol group.

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8. A process according to claim 1, wherein R^1 , R^2 , R^3 , R^4 , R^5 or R^6 each represents a methyl group, an ethyl group, an n-propyl group, an isopropyl group, an n-butyl group, an isobutyl group, a sec-butyl group, a t-butyl group, an n-pentyl group, an isopentyl group, a neopentyl group, a hexyl group, a heptyl group, an octyl group, a 2-ethylhexyl group, a nonyl group, a decyl group, an undecyl group, a dodecyl group, a trifluoromethyl group, a trifluoroethyl group, a trifluoropropyl group, a pentafluorobutyl group, a heptafluoropentyl group, a nonafluorohexyl group, a phenyl group, a vinyl group or a hydrogen atom, and

Z represents a methyl group, an ethyl group, an n-propyl group, an isopropyl group, an n-butyl group, an isobutyl group, a sec-butyl group, a t-butyl group, an n-pentyl group, an isopentyl group, a hexyl group, a heptyl group, an octyl group, a 2-ethylhexyl group, a nonyl group, a decyl group, an undecyl group, a dodecyl group, a trifluoromethyl group, a trifluoroethyl group, a trifluoropropyl group, a pentafluorobutyl group, a heptafluoropentyl group, a nonafluorohexyl group, a trimethylsilylethyl group, a trimethylsilylmethyl group or a hydrogen atom.

9. A process according to claim 1, wherein the polymerizable monomer represented by formula (1) is at least one selected from the group consisting of pentamethyldisiloxanylmethyl methacrylate, pentamethyldisiloxanylmethyl acryl-

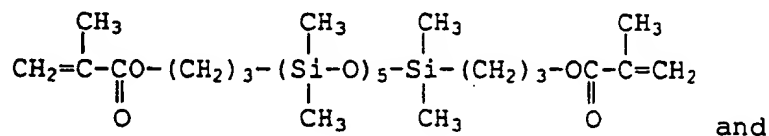
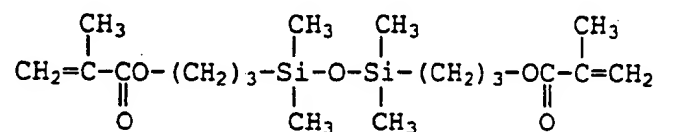
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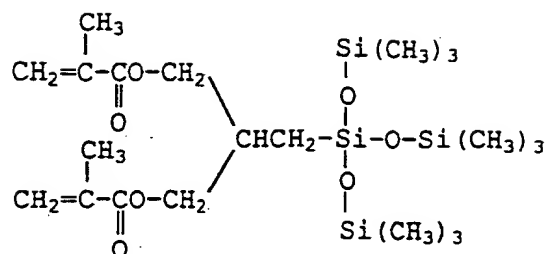
ate, pentamethyldisiloxanylpropyl methacrylate, pentamethyldisiloxanylpropyl acrylate, methylbis(trimethylsiloxy)silylpropyl methacrylate, methylbis(trimethylsiloxy)silylpropyl acrylate, tris(trimethylsiloxy)silylpropyl methacrylate, tris(trimethylsiloxy)silylpropyl acrylate, (3,3,3-trifluoropropyldimethylsiloxy)bis(trimethylsiloxy)silylmethyl methacrylate, (3,3,3-trifluoropropyldimethylsiloxy)bis(trimethylsiloxy)silylmethyl acrylate, (3,3,4,4,5,5,5-heptafluoropentyldimethylsiloxy)-(methylbis(trimethylsiloxy)siloxy)trimethylsiloxypropyl methacrylate and (3,3,4,4,5,5,5-heptafluoropentyldimethylsiloxy)(methylbis(trimethylsiloxy)siloxy)trimethylsiloxypropyl acrylate.

10. A process according to claim 1, wherein R⁷ represents a methyl group, an ethyl group, an n-propyl group, an isopropyl group, an n-butyl group, an isobutyl group, a sec-butyl group, a t-butyl group, an n-pentyl group, an isopentyl group, a hexyl group, a heptyl group, an octyl group, a 2-ethylhexyl group, a nonyl group, a decyl group, an undecyl group, a dodecyl group, a trifluoromethyl group, a trifluoroethyl group, a trifluoropropyl group, a pentafluorobutyl group, a heptafluoropentyl group, a nonafluorohexyl group, a fluorine atom or a hydrogen atom, and
- R⁸ represents a hydrogen atom, a methyl group, an ethyl group, an n-propyl group, an isopropyl group, an n-butyl group, an isobutyl group, a sec-butyl group, a t-butyl group, an n-pentyl group, an isopentyl group, a hexyl group, a heptyl group, an octyl group, a 2-ethylhexyl group, a nonyl group, a decyl group, an undecyl group, a dodecyl group; or a trifluoromethyl group, a trifluoroethyl group, a trifluoropropyl group, a pentafluorobutyl group, a heptafluoropentyl group or a nonafluorohexyl group each of which is bonded through a divalent hydrocarbon group with 1-4 carbon atoms; or a cyclohexyl group, a benzyl group or an isobornyl group.

11. A process according to claim 1, wherein the polymerizable monomer represented by formula (2) is at least one selected from the group consisting of 2,2,2-trifluoroethyl methacrylate, 2,2,2-trifluoroethyl- α -fluoroacrylate, 2,2,2-trifluoroethyl- α -trifluoromethyl acrylate, 2,2,3,3-tetrafluoropropyl methacrylate, 2,2,3,3,3-pentafluoropropyl methacrylate, 2,2,2,2',2',2'-hexafluoroisopropyl methacrylate, 2,2,3,4,4,4-hexafluorobutyl methacrylate, 2,2,3,3,4,4,5,5-octafluoropentyl methacrylate, 2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl methacrylate, 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl methacrylate, 2,2,3,3-tetrafluoro-1-methylpropyl methacrylate, 2,2,3,3-tetrafluoro-1,1-dimethylpropyl methacrylate, 2,2,3,3,4,4,5,5-octafluoro-1,1-dimethylpentyl methacrylate, methyl methacrylate, methyl acrylate, ethyl methacrylate, ethyl acrylate, isopropyl methacrylate, isopropyl acrylate, n-butyl methacrylate, n-butyl acrylate, t-butyl methacrylate, t-butyl acrylate, cyclohexyl methacrylate, cyclohexyl acrylate, benzyl methacrylate, benzyl acrylate, isobornyl methacrylate and isobornyl acrylate.

12. A process according to claim 1, wherein the crosslinkable monomer is at least one selected from the group consisting of ethylene glycol dimethacrylate, diethylene glycol dimethacrylate, propylene glycol dimethacrylate, 1,4-butanediol dimethacrylate, neopentyl glycol dimethacrylate, trimethylolpropane trimethacrylate and bisphenol A dimethacrylate; and siloxanyl dimethacrylates of





13. A process according to claim 1, wherein copolymerization ratio of the polymerizable monomer(s) represented by formula(e) (1) and/or (2) and the crosslinkable monomer is 99.5/0.5 to 5/95 in terms of weight ratio.
14. A process according to claim 1, wherein copolymerization ratio of the polymerizable monomer(s) represented by formula(e) (1) and/or (2) and the crosslinkable monomer is 99/1 to 10/90 in terms of weight ratio.
15. A process according to claim 1, wherein the volatile organic solvent is a solvent having a boiling point of 150°C or lower and selected from the group consisting of n-pentane, n-hexane, n-heptane, 2-methylhexane, 2,4-dimethylpentane, cyclopentane, methylcyclopentane, 1-hexene, 1-heptene, cyclohexene, benzene, toluene, dichloromethane, chloroform, carbon tetrachloride, fluorobenzene, hexafluorobenzene, diethyl ether, diisopropyl ether, ethyl vinyl ether, tetrahydrofuran, ethyl acetate, n-propyl acetate and n-butyl acetate.
16. A process according to claim 1, wherein the volatile organic solvent is used in an amount of 5-200 parts by weight based on 100 parts by weight of all monomer component.
17. A highly oxygen permeable polymer obtained by the process as claimed in claim 1.

18. A contact lens obtainable by a process according to claim 1.
19. An intraocular lens obtainable by a process according to claim 1.
- 5 20. A preformed polymer having excellent processability properties obtainable by a process according to claim 1.

INTERNATIONAL SEARCH REP

International Application No

PCT/JP 93/00635

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 G02B1/04; C08F230/08		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	G02B ; C08J ; C08F	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	US,A,4 110 264 (CHARLES W. NEEFE) 29 August 1978 see claims 1-5 see column 3, line 9 - line 20 ---	1
A	US,A,4 604 440 (OTTO WICHTERLE) 5 August 1986 see claims 1,4,5,11 see column 3, line 19 - line 48 ---	1
A	US,A,4 613 657 (TADASHI NARITA) 23 September 1986 see claims 1,5-10 see column 2, line 16 - line 68 see column 3, line 31 - line 42 ---	1
A	US,A,3 350 216 (DONALD E. MC VANNEL) 31 October 1967 see claim 1 -----	1
<p>⁹ Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"A" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
15 SEPTEMBER 1993		27. 09. 93
International Searching Authority		Signature of Authorized Officer
EUROPEAN PATENT OFFICE		DEPIJPER R.D.C.

Form PCT/ISA/210 (second sheet) (January 1985)

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

JP 9300635
SA 73525

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		DE-A,C 3512256	17-10-85
		FR-A- 2562547	11-10-85
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		JP-A- 60248717	09-12-85
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		DE-B- 1240280	
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